

CLAIMS

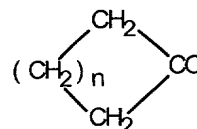
1. A process for oxidizing organic compounds comprising:
 contacting, in a zone of reaction, an oxidizable organic compound with a
 peroxide selected from the group consisting of hydrogen peroxide and organic
 5 hydroperoxides, in the presence of a catalytically effective amount of an insoluble
 catalyst comprising silicon oxide and an oxide of at least one peroxide-activating
 metal prepared by sol-gel techniques, wherein said catalyst is characterized by
 (i) the silicon to peroxide-activating atomic ratio is less than 10,000 to 1; (ii) is
 x-ray amorphous; (iii) possesses a Si-C infrared band; and (iv) has a surface area
 10 greater than 500 m²/g, a pore volume greater than 0.5 mL/g and an average pore
 diameter of greater than 4 nm.

2. The process of Claim 1 wherein the organic compound is selected
 from the group consisting of:

(a) cyclic olefins and olefins according to the formula

15 $R^1R^2C=CR^3R^4$,

wherein R¹, R², R³ and R⁴ are each independently -H; alkyl,
 wherein the alkyl group has from 1 to 16 carbon atoms; alkylaryl, wherein the
 alkylaryl group has from 7 to 16 carbon atoms; cycloalkyl, wherein the cycloalkyl
 group has from 6 to 10 carbon atoms; or alkylcycloalkyl, wherein the
 20 alkylcycloalkyl group has from 7 to 16 carbon atoms; and wherein said olefin can
 optionally containing halogen atoms;



(b) cyclic ketones according to the formula
 wherein n is an integer from 2 to 9;

(c) compounds of the formula C₆H₅R⁵, wherein R⁵ is -H, -OH; C₁
 25 to C₃ straight chain, saturated or unsaturated hydrocarbon radicals, -CO₂H; -CN;
 -COC_m, wherein m is an integer from 1 to 6; -OC_m, wherein m is an integer from
 1 to 6; or NR⁶R⁷, where R⁶ and R⁷ are each independently -H or C₁ to C₃ alkyl
 groups;

(d) alicyclic hydrocarbons according to the formula R⁸R⁹CH₂,
 30 wherein R⁸ and R⁹ together form a link of (-CH₂-)_p,
 wherein p is an integer from 4 to 11;

(e) aliphatic hydrocarbons of the formula C_qH_{2q+2}, wherein q is an
 integer from 1 to 20; and

(f) alcohols according to the formula R¹⁰R¹¹CHOH, wherein R¹⁰
 35 and R¹¹ are each independently -H; alkyl, wherein the alkyl group has from 1 to
 16 carbon atoms; alkylaryl, wherein the alkylaryl group has from 7 to 16 carbon

atoms; cycloalkyl, wherein the cycloalkyl group has from 6 to 10 carbon atoms; cycloalkyl wherein R^{10} and R^{11} taken together form a link containing 4 to 11 $-CH_2-$ groups; or alkylcycloalkyl, wherein the alkylcycloalkyl group has from 7 to 16 carbon atoms.

5 3. The process of Claim 1 wherein the peroxide-activating metal is selected from the group consisting of silver, cobalt, cerium, manganese, iron, copper, molybdenum, tungsten, vanadium, titanium, chromium and mixtures thereof.

10 4. The process of Claim 3 wherein the peroxide-activating metal is tetrahedrally coordinated titanium.

5. The process of Claim 1 wherein the catalyst is an amorphous titania/silica aerogel wherein the weight ratio of TiO_2 to SiO_2 is between 0.0005:1 and 0.5:1.

15 6. A process for the preparation of an aerogel catalyst comprising oxides of silicon and a peroxide-activating metal comprising:

- (i) preparing a sol-gel containing silicon and a peroxide-activating metal;
- (ii) extracting the gel with a solvent to remove substantially all of the water from the gel and optionally removing the solvent;
- 20 (iii) washing the gel with a solvent for the silylating agent;
- (iv) treating the gel with a silylation agent;
- (v) drying the treated gel at a temperature of from about ambient to about $130^{\circ}C$; and, optionally,
- (vi) calcining the gel,
- 25 at a temperature of less than about $400^{\circ}C$.

7. The process of Claim 6 wherein the silicon in step (i) is in the form of a silicate selected from the group consisting of $Si(OR^{12})_4$ and $SiR^{14}(OR^{13})_3$ where R^{12} is a C_1 to C_4 alkyl group, R^{13} is a C_1 to C_8 alkyl group and R^{14} is H, C_6H_5 or R^{13} , where C_6H_5 is a phenyl group.

30 8. The process of Claim 6 wherein the peroxide-activating metal is selected from the group consisting of silver, cobalt, cerium, manganese, iron, copper, molybdenum, tungsten, vanadium, titanium, chromium and mixtures thereof.

9. The process of Claim 6 wherein the silylating agent is selected from the group consisting of organosilanes, organosilylamines and organosilazanes.

10. The process of Claim 9 wherein the silylating agent is selected from the group consisting of chlorotrimethylsilane $((CH_3)_3SiCl)$, dichlorodimethylsilane $((CH_3)_2SiCl_2)$, bromochlorodimethylsilane $((CH_3)_2SiBrCl)$, chlorotriethylsilane $((C_2H_5)_3SiCl)$, chlorodimethylphenylsilane

- $((\text{CH}_3)_2\text{Si}(\text{C}_6\text{H}_5)\text{Cl})$, 1,2-diethyldisilazane ($\text{C}_2\text{H}_5\text{SiH}_2\text{NHSiH}_2\text{C}_2\text{H}_5$),
 1,1,2,2-tetramethyldisilazane ($((\text{CH}_3)_2\text{SiHNHSiH}(\text{CH}_3)_2)$),
 1,1,1,2,2,2-hexamethyldisilazane ($((\text{CH}_3)_3\text{SiNHSi}(\text{CH}_3)_3)$),
 1,1,2,2-tetraethyldisilazane ($(\text{C}_2\text{H}_5)_2\text{SiHNHSiH}(\text{C}_2\text{H}_5)_2$) and
 5 1,2-diisopropyldisilazane ($((\text{CH}_3)_2\text{CHSiH}_2\text{NHSiH}_2\text{CH}(\text{CH}_3)_2)$).
11. The process of Claim 9 wherein the silylating agent is selected from the group consisting of the silazanes and N,O-bis(trimethylsilyl)trifluoroacetamide ($\text{CF}_3\text{C}(\text{OSi}(\text{CH}_3)_3)=\text{NSi}(\text{CH}_3)_3$).
12. The process of Claim 6 wherein the water is removed in step ii by
 10 either a protic solvent or an aprotic solvent.
13. The process of Claim 12 wherein the protic solvent is alcohol.
14. The process of Claim 12 wherein the aprotic solvent is selected from the group consisting of acetone and tetrahydrofuran.
15. A catalyst composition comprising silica and an oxide of at least one peroxide-activating metal characterized by:
- (i) having a silicon to peroxide-activating atomic ratio of less than 10,000 to 1;
 (ii) being x-ray amorphous;
 (iii) possessing a Si-C infrared band; and
 20 (iv) having a surface area greater than $500 \text{ m}^2/\text{g}$, a pore volume greater than 0.5 mL/g and an average pore diameter of greater than 4 nm .
16. The process of Claim 15 wherein the peroxide-activating metal is selected from the group consisting of silver, cobalt, cerium, manganese, iron, copper, molybdenum, tungsten, vanadium, titanium, chromium and mixtures
 25 thereof.